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THE PHYSICAL PROPERTIES OF INTERMETALLIC COMPOUNDS
OF FIXED COMPOSITION

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[Tables and figures referred to are appended.]

Introduction

This work investigates the mechanism of conductivity in the intermetallic phase of fixed composition Mg_3Sb_2 . On the basis of the data obtained a conclusion is reached concerning the semiconductivity of Mg_3Sb_2 .

It is customary to distinguish several types of intermetallic compounds. First, intermetallic chemical compounds of constant, or fixed, composition are Daltonides, according to the terminology of Kurnakov [1]. Daltonides are formed in accordance with normal chemical valency of the components and possess a crystalline structure characteristic of compounds with heteropolar and homeopolar chemical bonds. To compounds of this type there corresponds, on the isotherms of the constitution-property diagram, a rather sharply-expressed singular point due to the structure of the crystalline lattice, which (structure) is distinguished from the structures of intermediate alloys.

The second group of typical intermetallic compounds is formed by so-called "electron compounds" or phases of Yum-Rozeri [2]. Compounds of this type are characterized by a definite value for the ratio of the number of valence electrons to the total number of atoms in the "cell." These electron-atom ratios, which can be called "the alloy valences," vary with the composition of the phases in certain limits [3, 4].

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The Yum-Rozeri rule can apparently be described as a free-forming valence rule for intermetallic compounds with a mainly metallic bond which is realized by way of a collectivization of the valence electrons belonging to the atoms of the components making up the alloy. However, in these alloys exists heteropolarity, whose influence cannot be disregarded. This follows from considerations first indicated by Dehlinger [5]. Intermetallic compounds of the Yum-Rozeri type are exceptional cases of the most common type of chemical compounds of fixed composition, that is, phases with a wide region of existence on constitution diagrams (bertollides).

To the third group of chemical intermetallic compounds belong compounds with an obscure regularity of composition. In these compounds, the rule of normal valence and the constancy of the ratios of the number of valence electrons to the number of atoms in the elementary cell are not observed.

Intermetallic compounds of fixed composition with stoichiometric formulas, constructed according to the rules of valence in classical chemistry, are formed only among metals standing on both sides of the so-called "Zintl" boundary [6], lying between the true metals and the anion-formers. The valence metallic compounds are formed where the negative valence of the anion does not exceed four. Such compounds are crystallized in structures characteristic of compounds with ionic or co-valence bond and are characterized by small coordination numbers; that is, incomplete packing of atoms. Besides many sulfides, selenides, and tellurides, to such compounds belong, for example, AlAs, InSb, GaP, GaSb and others with lattices of the zinc blende type; SnSb, SnAs with the lattice of rock salt; Mg_2Si , Mg_2Ge , Mg_2Sn and others with the structure of anti-isomorphic fluorspar; $PtAs_2$, $AuSb_2$, $PdAs_2$, $PtSb_2$ and others with a cubic lattice, namely Mg_3N_2 , Mg_3As_2 , Mg_3P_2 , and with a hexagonal lattice like Mg_3Sb_2 and Mg_3Bi_2 , which are anti-isomorphic to the oxides Sc_2O_3 and La_2O_3 . Therefore, only in the structure of the fluorspar type is homeopolar valence of silicon and others equal to the coordination number of these atoms, that is, to four. It is only in this case that pure homeopolar spin bonds are possible.

In all other cases, "salt-forming" structures indicate that atoms are overcharged by transition of electrons to anion-formers As, Sn, Sb, Bi, and others, with the formation, at least partially, of ionic bonds. Especially clear is the heteropolarity of the valence compounds of alkali and alkaline-earth metals possessing a strong tendency to the formation of positive ions. Examples are Li_3Bi , Cs_3Sb , Na_3Bi , Ca_2Sn , and others.

Metallic phases with heteropolar bonds differ significantly from salt-like heteropolar compounds. Among these latter, the Coulomb forces between ions are the most significant forces of the chemical bond. The dispersion forces added to these forces play an insignificant role [7]. In consequence of this, neutral atoms located between ions are bound weakly and therefore are stable for only very insignificant deviations from the stoichiometric composition depending upon the normal valence of ions. However, intermetallic heteropolar phases in solid compositions observe rather large regions of homogeneity; that is, deviations from stoichiometric composition.

Dehlinger [8] formulated conditions governing the formation of heteropolar metallic compounds.

In general, the stability of such compounds is greater the more electropositive the metal and the more electronegative the anion-formers.

The zone theory of solids draws a sharp line between metals and other conductors of electricity. The presence of an unfilled band or overlapping band of energy levels in metals does not require expenditure of energy for the emergence of conduction electrons. The electrical conductivity of metals increase in temperature because of the decreasing influence of thermal motion of the lattice upon the mobility of the conduction electrons. The amount of the residual resistance in metals is smaller the purer the metal and the less the influence of admixed atoms. The electrical conductivity of semiconductors for absolute temperature equal to zero is absent, because the presence in the atomic structure of a band of valence electrons and the

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A semiconductor mechanism of conductivity, connected with the passage of electrons from the filled band to the conductivity zone, becomes noticeable only for high temperatures, the higher the greater the initial concentration of "metallic" electrons (or holes) in the sample.

It is necessary to consider semiconductors of such a nature as an example of an additive structure of semiconductive mechanism plus metallic mechanism. The existence of the forbidden zone in the energy spectrum of a crystal is masked by the "metallic" electrons of the atoms of the admixture, whose (atoms) number even for a deviation from stoichiometry of the order of 0.01 atomic percent exceeds the number of thermally-excited electrons of the basic lattice of the crystal. Only for comparatively high temperatures does the ratio sharply decrease: the number of thermally-excited electrons is many times greater than the number of electrons of the admixed atoms, and the exponential dependence of electrical conductivity upon temperature permits one to determine the width of the forbidden zone. Roughly speaking, these semiconductors behave at low temperatures as metals and at high temperatures as semiconductors. (For data on Ge and Si, examples of the type of semiconductors described, see Item 16 in the Bibliography.)

In any case chemical compounds possess smaller electrical conductivity the more they are saturated and the narrower the region of homogeneity on the constitution diagram, that is, the more accurately they follow the rule of multiple proportion. Any deviation of this kind is a necessary condition for the appearance of electrical conductivity. The degree of departure from the rule of multiple proportion in typical ions and homeopolar compounds increases with increase in temperature. Intermetallic alloys even at low temperatures are characterized by noticeable deviations from the rule of multiple proportions, which fact is completely regular if one keeps in mind the nature of the forces of chemical interaction acting in them.

As already indicated, intermetallic compounds with normal valence must probably be considered as a transition from (a) normal valence compounds, with a narrow region of possible deviations from stoichiometry to (b) compounds formed by metals with weak anion-formers, with wider boundaries of deviation from stoichiometry.

The mechanism of conductivity in such alloys is insufficiently clear. The aim of the present work is to attempt to analyze this problem.

It was possible to assume a-priori that intermetallic compounds of this class are typical semiconductors, characterized by the presence of a forbidden zone in the crystal's system of energy levels.

The problem of the width of the forbidden zone, the character of the distribution of admixed levels, and the determination of the concentration of the electrons of the admixture and of the electrons of the basic lattice of the compound can be solved only by the introduction of measurements of such quantities as electrical conductivity, Hall effect, thermoelectromotive force, internal photoeffect, and others in a wide interval of temperatures. These are determined by the experimental side of the work.

Selection of Material for Investigation

The object selected for investigation was the intermetallic compound of fixed composition Mg_3Sb_2 . The position of this substance in the general system of magnesium compounds is well illustrated in Table 1, a collated table borrowed by us from a survey article by Laves [12].

The elements with respect to the right side of "Zintl's boundary" (that is, anion-formers) give, along with Mg, compounds having only valence composition with crystalline structures characteristic of typical salt-forming compounds. On the other hand, elements located left of this boundary form, with Mg (besides Mg_5Ge_2 ,

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Mg_5In_2 and Mg_5Tl_2), compounds of rather chance stoichiometric composition, which (compounds) possess structures like that of metals and true alloys.

The ion bond in Mg_3Sb_2 is sharply expressed, although Sb is an anion-former naturally very much weaker than, say, S or Se. (The bond in Mg_2Sn and other compounds of the IV group are no longer purely ionic. Here, probably, the essential role is played by the usual spin bond, increasing from Mg_2Si to Mg_2Pb). The constitution diagram of alloys of Mg with Sb is shown in Figure 1 [13]. Mg_3Sb_2 with surplus Mg forms composite crystals and exists in two modifications. The alpha \rightleftharpoons beta conversion of Mg_3Sb_2 is observed between 40 and 44 percent Sb, according to the pause on the cooling curve for 930 degrees plus or minus 2 degrees centigrade. From the side of surplus Sb, Mg_3Sb_2 apparently does not form composite crystals. The beta-modification of Mg_3Sb_2 is stable for high temperatures and is still less "metallic" according to its properties than the alpha-modification. This is indicated by the high melting point and large heat of formation, reaching 13.7 calories/gram · mole, and also by the lattice structure. According to Zintl and Husemann [13], alpha- Mg_3Sb_2 possesses the trigonal A-structure of lanthanide sesquioxide; but beta- Mg_3Sb_2 possesses the cubic structure of lanthanide sesquioxide. From the constitution diagram it follows that the chemical composition of Mg_3Sb_2 is stable and practically does not dissociate during melting to the atoms of the elements. Alloys right and left of the pure chemical composition differ sharply from each other: on the left there are no free atoms of Sb, and on the right there are no free atoms of Mg.

Method of Operation

In order to investigate the electrical properties of the compound Mg_3Sb_2 , we strove to prepare samples of alloys with the composition corresponding as closely as possible to stoichiometry. In the first trials, the samples were generally prepared by melting Sb and Mg in crucibles of electrographite or very pure Acheson graphite under a layer of graphite powder. The heating was carried out in large molybdenum furnaces in an atmosphere of dry argon. The melting of Mg and Sb, according to the instructions of Grube and Bornhax [14], was carried out thus: the crucible was first filled with pieces of Mg and after that it was covered on top with Sb. During heating of the crucible, the Sb begins to melt first of all and flows into the interstices between the Mg, slowly reacting with the Mg pieces. In the opposite case, the reaction goes very violently, with ejection of part of the fused masses. Next, because of the evolution of much heat of reaction, the Mg is fused and the reaction proceeds to completion. Here the product of reaction remains solid and fuses only for considerably higher temperatures.

Obtaining an alloy with a composition close to Mg_3Sb_2 was hampered by the fact that one of the components, usually Mg, was slightly burned out in the melting process.

With the object of obtaining quite homogeneous samples, we placed the alloys in iron crucibles in an atmosphere of argon or nitrogen. A slow increase in temperature up to 1,400-1,500 degrees centigrade was effected in the course of 8-10 hours, and after that the alloy was allowed to cool for 6-8 hours. We succeeded in obtaining rather homogeneous coarse polycrystalline samples. The samples for investigation of electrical properties were prepared from the alloy by sawing in the form of small parallelepipeds or were pressed from crushed alloy in a special form under pressures from 250 to 2,000 kilograms per square centimeter.

In order to eliminate nonhomogeneities the prepared samples were made homogeneous by annealing in evacuated glass ampoules made of hard glass at a temperature 500-600 degrees centigrade for 10 to 12 hours. Part of the samples were annealed for longer periods of up to 2 days.

The homogeneity of the samples was verified by chemical analysis and by study of microsections under a metallo-microscope.

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We have made attempts to group coarse monocrystals of the compounds Mg_3Sb_2 according to Obreimov's method. Tubes with conical ends were prepared by us from quartz, graphite and iron. However, our attempts ended unsuccessfully. Invariably we obtained coarse granular crystallites.

Magnesium for the preparation of the samples was triple-sublimated in vacuo. The content of admixture in them did not exceed 0.05 percent. Two kinds of antimony were used, Chinese and Kalbaum. The content of impurities in both did not exceed 0.17 percent. (A. P. Obukhov, Chemical Laboratory, Leningrad Physical Technical Institute, assisted in these analyses.) The samples prepared for measurements were kept in evacuated glass ampoules or in a desiccator with P_2O_5 or $CaCl_2$ to preserve them from oxidation and the action of water vapor.

In 20-x microphotographs of microsections of Mg-Sb alloys of different constitution (40 percent Sb, 60 percent Mg, and 75.25 percent Sb, 24.75 percent Mg) were clearly visible crystals of Mg_3Sb_2 , the number of which increases in the visual field with the approach of the alloy's composition to the composition of the compound.

Measuring Methods

Measurement of the temperature behavior of electrical conductivity cannot fully represent the mechanism of current transmission in matter. The sign of the charge carriers, their concentration and mobility at a given temperature can be determined by the simultaneous measurement of the Hall effect and thermoelectromotive force.

The method of measurement of electrical conductivity and thermo-EMF is the usual compensation method. The sample, placed in special holders, was heated above room temperature in an oven, the temperature of which was maintained constant with an accuracy of plus or minus 0.5 degrees centigrade by means of a thermocouple and thyatron thermo-regulator. Measurements at low temperatures were carried on down to minus 183 degrees centigrade. The samples fastened in the holders were placed in a closed glass or metallic test tube sunk into a Dewar flask with liquid oxygen or cooled by benzol or ethyl alcohol. The temperature was measured by a copper-constantan thermocouple pressed against the sample. For the measurement of thermoelectromotive force a differential thermocouple was used.

The Hall effect was measured with a constant direct current. The scheme of measurement was a compensation scheme. Since preliminary measurements indicated the independence of the Hall constant upon magnetic field strength, the measurements were generally carried out for field strengths equal to 10,000 to 13,500 oersteds. For the measurement of the Hall effect at low temperatures a special flat Dewar flask was made, which was placed in a pole gap 2.5 centimeters wide. The sample in this case was immersed directly in the cooled liquid or placed in a test tube made of thin copper foil.

Dependence of Specific Electrical Conductivity Upon Temperature

From a great number of prepared samples more than 25 samples of alloys with composition close to the stoichiometric compound Mg_3Sb_2 were measured in detail. In Figures 2, 3, 4, 5 are given curves showing the temperature behavior of electrical conductivity for some samples. On the ordinate axis is placed the logarithmic value of electrical conductivity; on the abscissa is $1000/T$, where T is absolute temperature. The measurements of electrical conductivity were made in the interval from minus 160 degrees centigrade to plus 350 (or 400) degrees centigrade. Some samples were studied up to 600 degrees centigrade. For several samples, the composition according to the data of chemical analysis and the values of specific electrical conductivity at 20 degrees centigrade are shown in Table 2.

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The curves of Figure 2 show that with increase in deviation of the alloy from the composition corresponding to the compound Mg_3Sb_2 the specific electrical conductivity of the alloy increases. A similar dependence is illustrated in Figures 3, 4, 5. It is necessary to note that the data of chemical analysis is obtained for averaged tests made on a bar of the alloy, and not for the given measured sample; therefore, it is impossible to expect a more accurate relation between specific electrical conductivity and composition. The samples sawn from the bars gave significantly larger scatter in the values of both electrical conductivity and other properties (thermoelectromotive force and the Hall effect) than samples compressed from alloys ground to a powder and then homogenized by prolonged annealing at high temperatures in vacuo. The prolonged annealing, as a rule, increased the electrical conductivity of a sample approximately by one order of magnitude without changing the temperature coefficient $d\sigma/dT$ essentially.

Successive heating and cooling of the sample did not cause further irreversible variation in electrical conductivity. Such a phenomenon is observed also in other semiconductors, during the pressing and c. inkering of samples prepared from fine crystals, and is connected obviously with variations in the conditions governing the contact of individual crystals with each other. The electrical conductivity of the samples under investigation varied from 10^2 to 10^{-5} /ohm·cm. The magnitude and sign of the temperature coefficient of electrical conductivity also varied in wide intervals. Among samples of poorly conducting alloys at low temperatures, a small positive temperature behavior of electrical conductivity with increase in temperature is replaced by a rapid increase in σ , following the ordinary exponential law of increase of electrical conductivity with temperature among typical semiconductors. In this region of temperatures the dependences $\log \sigma = f(1/T)$ are straight lines. The tangent of the angle of inclination of these straight lines to the $(1/T)$ -axis, multiplied by k , must be equal to the chemical potential of the carriers that govern the conductivity of the substance (electrons or holes). For low temperatures this chemical potential approximately equals half the distance from the proper permissible band to the level of the admixtures. For low temperatures this equals half the total width of the forbidden zone of the crystal; that is, $\frac{1}{2} \cdot \Delta E$, where ΔE is the width of the zone.

With increase in content, in the sample, of a surplus, relative to the composition of the intermetallic compound Mg_3Sb_2 , of a metal, there is observed a gradual displacement of the region of inflexion toward the side of higher temperatures, which (displacement) is accompanied by a gradual decrease in the slope of the straight portions of the logarithmic curves.

The alloy samples with large excess of one component relative to the composition of the intermetallic compound are characterized by a gradual transition to a metallic type of conductivity with a negative temperature coefficient of electrical conductivity.

The width of the energy barrier surmountable by carriers of a charge for transition to the zone of conductivity (the work of dissociation of the charges), which (width) is determined from the slope of the logarithmic straight lines ($\log \sigma$, $1/T$) in the region of high temperatures, is shown for a number of samples in the sixth column of Table 2. The general behavior of the electrical conductivity with temperature for poorly-conducting samples of Mg_3Sb_2 can be represented by the binomial formula:

$$\sigma = A_1 e^{-\frac{\Delta E_1}{2kT}} + A_2 e^{-\frac{\Delta E}{2kT}} \quad (1)$$

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The first term, where A_1 and ΔE_2 are small ($A_1 \approx 2 \cdot 10^{-5}$ to $4 \cdot 10^{-2}$; $\Delta E_2 \approx 0.05$ to 0.10 eV), predominates for lower temperatures.

The second term, where ΔE_1 varies in the interval 0.36 - 0.72 eV and $A_2 \approx 1$ to 20 , predominates for higher temperatures.

Specially conducted tests on the electrolysis of alloys, carried out for temperatures from 20 to 350 degrees centigrade to determine the role of the ionic current in electrical conductivity, give reasons to affirm that the ionic part of sigma σ in each case is less than 0.1 percent. It is possible to consider that for all temperatures studied Mg_3Sb_2 is mainly an electron conductor.

The first term of Equation (1) in all probability corresponds to an admixture; the second, to the natural or "proper" conductivity (eigenconductivity) of the substance.

The Hall Effect

The temperature behavior of electrical conductivity is determined not only by measurement of the concentration of carriers with temperature, but also by measurement of their mobility. Study of the temperature dependence of the Hall constant permits one to determine the concentration of electrons in the zone of conductivity or of holes in the normal zone if one proceeds from the assumption that electrical conductivity is governed by carriers of just one sign whatever it may be.

Moreover, the sign of the Hall effect corresponds to the kind of charge carriers (electrons or holes), but in the case of composite conductivity it indicates the pre-eminent role of one or the other kind of carriers in the passage of the current.

Measurements of the Hall effect were made by us for direct current by means of an ordinary compensation scheme and covered an interval of temperatures from minus 170 to plus 350 degrees centigrade. The magnetic field strength was generally $8,000$ to $12,000$ oersteds.

The temperature dependence of the Hall constant R , represented on the coordinates $\log R$ and $1000/T$ for a number of samples, is shown in Figures 6, 7, 8. On the ordinate axis are also values of $\log n$, where n is the concentration of charge carriers calculated on the assumption that the total electrical conductivity is governed by the current carriers of just one sign. The constant of the Hall effect is expressed in units of $cm^3/abamp \cdot sec$. With increasing temperatures the Hall constant of all samples studied by us decreases. For low temperatures the slope of the curve ($\log R$, $1/T$) is small. This slope is proportional to ΔE_1 (or ΔE_2), where ΔE_1 is the depth of the levels of the surplus metal under the zone of conductivity (ΔE_2 is the height of the admixture levels upon the filled zone).

The small value of ΔE_2 indicates that the "admixture" levels in Mg_3Sb_2 lie close to the filled zone. The quantity ΔE_2 for samples with "hole" conductivity lies in the interval 0.015 to 0.06 eV; that is, of the order of kT for room temperatures. With increasing temperatures the slope of the curves ($\log R$, $1/T$) increases and the magnitude of the Hall constant clearly converges toward zero for temperatures 800 to $1,000$ degrees centigrade. In this region, Mg_3Sb_2 is a composite semiconductor, for which we have:

$$R = \pm \frac{3\pi}{8e} \frac{n_1 u_1^2 - n_2 u_2^2}{(n_1 u_1 + n_2 u_2)^2} \quad (2)$$

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where n_1 and n_2 are the concentrations of the free electrons and holes; u_1 and u_2 are their mobilities.

In the special case where $n_1 = n_2 = n$; that is, for a semiconductor with natural conductivity:

$$R = \pm \frac{3\pi}{8en} \frac{u_1 - u_2}{u_1 + u_2}, \quad (3)$$

that is, the variation of R is basically determined by the quantity n , which increases with temperature according to the following law:

$$n = n_1 = n_2 = \sqrt{u_1 u_2} \cdot e^{-\frac{\Delta E}{2kT}}. \quad (4)$$

Here

$$u_1 = 2 \left(\frac{2\pi m_1 kT}{h^2} \right)^{3/2} \quad \text{and} \quad u_2 = 2 \left(\frac{2\pi m_2 kT}{h^2} \right)^{3/2}$$

where m_1 and m_2 are the effective masses of the free electrons and holes, respectively. This case exists for high temperatures, when n is large in comparison with the concentration of admixed atoms.

Thus, the slope of the rectilinear part of the curve $(\log R, 1/T)$ in the region of natural conductivity must be proportional to ΔE , the width of the forbidden zone. The sign of R must be negative, since it follows from the theory of semiconductors that u_1 is greater than u_2 .

In our case the sign of the Hall constant for the whole temperature interval and for all samples studied corresponded to "hole" conductivity. Measurements at higher temperatures, where on the above-indicated basis one could have expected variations, or reversals, in the sign of the Hall effect, were not successfully effected by us because of a number of technical difficulties; measurements for such high temperatures would be of great interest since one could then give an accurate value for the width of the forbidden zone ΔE . On the basis of prolonged measurements this quantity can be determined only approximately with respect to the value dR/dT of the high-temperature portion of the curve.

In Table 3 are shown the values of ΔE_2 and ΔE for several samples defined graphically with respect to the temperature behavior of the Hall effect in the region of low and high temperatures.

As should be expected, ΔE determined from the Hall effect is of the same order as the value of ΔE calculated from the temperature behavior of electrical conductivity in the region of high temperatures.

The theoretical value of the energy jump ΔE for Mg_3Sb_2 , calculated by Kontorova with the approximation that the electrons be weakly bound, equals 1.08 eV.

The average length L_0 of free flight for charged carriers in the Mg_3Sb_2 phase can be evaluated with respect to experimental values of electrical conductivity, concentration of carriers, and ΔE . The electrical conductivity of an admixed semiconductor is:

$$\sigma = 0.024 l_0 \cdot n^{1/2} \cdot T^{1/4} \cdot e^{-\frac{\Delta E}{2kT}} \text{ ohm}^{-1} \cdot \text{cm}^{-1}. \quad (5)$$

Consequently, we have for the average free length:

$$l_0 = \frac{\sigma \cdot e^{\frac{\Delta E}{2kT}}}{0.024 \cdot n^{1/2} T^{1/4}} \text{ cm}. \quad (6)$$

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For samples No 7 (VII), 6 (VI), and 3 (VII), the calculated values of L_0 at 20 degrees centigrade turn out to equal, respectively, $3 \cdot 10^{-6}$, $4 \cdot 10^{-6}$, and $1.2 \cdot 10^{-6}$ centimeters.

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These values must be considered somewhat excessively large, since the concentration of carriers according to the Hall effect is determined on the assumption of only one sign of the carriers.

We shall show that the length of free flight, or path, in pure samples of Ge is $5 \cdot 10^{-6}$ to $10 \cdot 10^{-6}$ centimeters, but for pure Si it is $1 \cdot 10^{-6}$ to $2.9 \cdot 10^{-6}$ centimeters [15]. Both of these elements are typical admixed semiconductors.

The mobility of the charge carriers, for a given temperature T , of a semiconductor with a single mechanism of conductivity is:

$$\mu = \frac{4}{3} \frac{e l_0}{(2 \pi m k T)^{1/2}} \frac{\text{cm}^2}{\text{volt} \cdot \text{sec}} \quad (7)$$

and is determined experimentally as the product of the Hall effect constant and electrical conductivity σ ; that is:

$$\mu = \frac{8}{3 \pi} \sigma R \frac{\text{cm}^2}{\text{volt} \cdot \text{sec}} \quad (8)$$

If the average length L_0 of free flight (path) is determined only by the scattering of the electron waves on lattice oscillations, then L_0 varies inversely proportionally to temperature, but the dependence of mobility upon temperature in this case will be:

$$\mu = \frac{C}{T^{3/2}} \quad (9)$$

where C is a constant.

At low temperatures a notable role begins to be played by scattering upon the admixed atoms ("impurities") and upon other nonhomogeneities in the lattice, which scattering is proportional to the concentration of the admixture and slightly dependent upon temperature, decreasing the mobility according to a $3/2$ law.

In the case of composite ("additive") conductivity, comparison of theory with experiment is quite complicated, since in the conductivity process both mechanisms (electron and hole) are combined, while in the Hall phenomena and thermoelectromotive force part corresponding to the two forms of carriers they are separate.

If one employs Formula (8) for calculations, then for various samples of the Mg_3Sb_2 phase the mobility (at 20 degrees centigrade will vary in a wide interval from 0.01 to 50 $\text{cm}^2/\text{volt} \cdot \text{sec}$. As for the temperature behavior of mobility only certain samples possess an approximate correspondence with elementary theory (see, for example, the curve for sample No 5 in Figure 9); for most samples the temperature dependence of mobility is of quite another form (see the curves for samples No 3 (V) and 3 (VII) in Figure 9). The very small values of mobility as obtained by calculation are probably governed by the composite conductivity of the Mg_3Sb_2 phase.

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Thermoelectromotive Force

The thermoelectromotive force of Mg_3Sb_2 was measured relative to slow electrons in the temperature range from -170 degrees centigrade to +600 degrees centigrade. The temperature difference at the end of a sample was determined by a differential thermocouple and was 10 to 20 degrees centigrade. Thermoelectromotive force and temperatures of a sample were measured by Feysner's compensator.

Most of the alloy samples prepared close to the Mg_3Sb_2 composition indicated a "hole" nature, and only several samples indicated an electron nature (curves of samples No 7 and 17 in Figure 10).

Samples with poor conductivity (0.0008 to 0.00002/ohm-cm) are characterized by a temperature dependence of thermoelectromotive force, which is in rather good agreement with theory. The thermoelectromotive forces of these samples decrease with increase in temperature, according to the equation,

$$\alpha = \pm \frac{k}{e} \lg \frac{n_0}{c} - \frac{\Delta E}{2eT} \quad (10)$$

which represents the temperature dependence of the thermoelectromotive force of a semiconductor with a single kind of charge carriers.

Here n_0 is the concentration of charge carriers in a semiconductor for T approaching infinity; c is the concentration of electrons in a metal; ΔE is the work of dissociation of the carriers in a semiconductor.

For samples No 9 and 7 the quantity ΔE , defined graphically from the temperature behavior of electrical conductivity, turned out to equal 0.42 and 0.44 eV respectively. The function $\alpha = f(T)$, computed from Formula (10), is shown in Figure 10 by dotted lines. As is seen, in the region of high temperatures the coincidence of the theoretical and experimental curves is rather satisfactory, keeping in mind the low accuracy of determination of ΔE . In the region of low temperatures, as to be expected, the experimental values of α are less than the theoretical ones because in this region an important role begins to be played by the atoms of the admixture with less work of dissociation.

The majority of samples well-homogenized by prolonged annealing show an anomalous behavior of thermoelectromotive forces: that is, increase in thermoelectromotive force with increasing temperature. The possible explanation of this fact shall be discussed later. The thermoelectromotive forces of such samples usually equal 20 to 80 microvolts per degree centigrade at -170 degrees centigrade and increases up to 450-600 microvolts per degree centigrade at 350 to 400 degrees centigrade. The thermoelectromotive forces of poorly-conducting samples of Mg_3Sb_2 at -130 degrees centigrade is of the order of 1.1 to 1.2 millivolts per degree centigrade and decreases to 300-350 microvolts per degree centigrade at 400 degrees centigrade. The variations in thermoelectromotive force with temperature are inverse. In Figure 11 are shown the values of thermoelectromotive force and electrical conductivity for various samples of Mg_3Sb_2 at 20 degrees centigrade.

Heat Conductivity

At our request, T. V. Klassen determined the thermal conductivities of several Mg-Sb alloy samples with a composition close to the stoichiometry of Mg_3Sb_2 .

Thermal conductivity was measured in four homogeneous samples. The coefficient of thermal conductivity was determined as the average of 6 to 8 measurements. In Table 4 are shown the electrical conductivity σ at 20 degrees centigrade and the thermal conductivity λ for the average temperature of

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a sample at 60 degrees centigrade. The temperature drop in a sample was generally 15 to 25 degrees centigrade. In Table 4 are shown for comparison the values σ and λ for pure Mg and Sb at room temperatures [16].

The maximum relative error in the determination of λ was 6 percent. Extrapolation of thermal conductivity to the value $\sigma = 0$ gave for the thermal conductivity of the lattice of pure Mg_3Sb_2 a quantity of the order of 0.0023 cal/cm-sec-°C.

Discussion of Experimental Data

Analysis of the experimental data permits one, as it seems to us, to make the following conclusions with sufficient grounds. The intermetallic compound Mg_3Sb_2 , a typical representative of constant-composition phases, is an admixed semiconductor according to its electrical properties.

The width of the forbidden zone in a system of energy levels of this compound equals 0.65 to 0.80 eV. The electrical conductivity of samples close in composition to the stoichiometry of Mg_3Sb_2 is from 10^{-4} to 10^{-5} /ohm-cm; that is, 10^9 to 10^{10} times less than the specific conductivity of the metals composing this compound. Small deviations from stoichiometry lead to a sharp variation in the electrical properties of the compound; that is, to an increase in electrical conductivity and a decrease in thermoelectromotive force. An excess of one or the other component causes local levels in the forbidden zone, which lie a small distance from the upper edge of the filled zone or two conductivity zones. Even a negligible admixture with concentrations 10^{-4} to 10^{-5} gives very much greater charge-carriers than it can give thermal excitation in the basic lattice of Mg_3Sb_2 . Only at very high temperatures does natural electrical conductivity begin. Parallel with electrical conductivity thermal conductivity varies also, equal, for pure Mg_3Sb_2 , to 0.0023 cal/cm-sec-°C which is 160 times less than the thermal conductivity of Mg. A small concentration of free charge carriers in Mg_3Sb_2 , determined from the Hall effect, is clearly insufficient for the creation of the metallic bond and cannot ensure the properties of a solid. The bond forces in this intermetallic compound possess another derivation coinciding with the valence bonds of ionic crystals. This is indicated by the structure of the compound, characterized (structure) by a small coordination number and by a high melting point and large heat of formation, reaching 13.7 kilocal/g mol. The overwhelming majority of semiconductors also possess heteropolar lattices constructed of positive metal and negative metal atoms. In the case of Mg_3Sb_2 , these are ions of Mg^{++} and Sb^{---} . In lattices of this type the internal potential is periodic and consequently the energy spectrum of electrons will represent a system of zones of various lagging parts.

Among the zones of the spectrum it will be possible to distinguish two types of zones: zones originating from terms of the metalloid atom and zones originating from terms of the metallic atom.

The distribution of electrons according to the terms in a magnesium atom are: $(1s)^2, (2s)^2, (2p)^6, (3s)^2$. In the antimony atom: $(1s)^2, (2s)^2, (2p)^6, (3s)^2, (3p)^6, (3d)^{10}, (4s)^2, (4p)^6, (4d)^{10}, (5s)^2, (5p)^3$.

In Mg_3Sb_2 crystals, zone (5p) of Sb lies directly under zone (3s) of Mg. In zone (3s) of Mg it would be necessary to distribute $3 \cdot 2N$ electrons, where N is the number of Mg_3Sb_2 molecules per unit volume. In zone (5p) of Sb there are $6 \cdot 2N = 12N$ places from which $3 \cdot 2N = 6N$ places are taken by electrons; these places are naturally filled by valence electrons passing from the higher (3s) zone of Mg. Thus zone (3s) remains quite empty and becomes a zone of conductivity, but zone (5p) of Sb turns out to be completely filled by electrons and represents a normal zone. The distribution of the valence electrons of Mg in the zone forming the term (5p) of Sb indicates the ionic character of the bond in the compound of Mg_3Sb_2 , where the role of the metalloid ion is played by Sb ---.

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For a more detailed discussion of the results of measurements let us turn our attention toward two peculiarities: (a) the anomalous behavior of thermoelectromotive force with temperature for most samples with hole conductivity, that is, increase in thermoelectromotive force with temperature (see "Thermoelectric Force"), and (b) very small values of hole mobility in a number of samples obtained (values) from measurements of electrical conductivity and the Hall effect.

Mobility of the order of 0.1 to 0.01 cm²/volt-sec is slightly probable for electrons and holes in a crystalline lattice, all the more so since values of mobility for holes of the order of 50 cm²/volt-sec were obtained at 20 degrees centigrade for a number of Mg₃Sb₂ samples.

We consider that the above-mentioned phenomena can be explained by the presence of composite conductivity.

The basis for such an assumption is a comparison of (a) experimental values of thermoelectromotive force in various Mg₃Sb₂ samples as a function of the concentration of charge carriers, determined (concentration) by Hall measurements, with (b) the theoretical curve $\alpha = f(\log n)$ calculated for an ionic semiconductor with a single sign of the charge carriers [17]:

$$\alpha = \pm \frac{k}{e} \int_{T_1}^{T_2} \left[2 + \ln \frac{2(2\pi m \pm kT)^{3/2}}{h^3 n \pm} \right] dT. \quad (11)$$

In Figure 12, line 1 is calculated from the formula. Departures from this straight line can be considered as an indication of the composite character of conductivity or the nonhomogeneous composition of the sample. Curves 2 and 3 are obtained for two Mg₃Sb₂ samples. At high temperatures, the experimental curves approximate the theoretical ones, which fact is revealed by the gradual increase in the role of only one kind of carriers (in our case, holes). The composite conductivity for obtaining such a deviation from the theoretical dependence $\alpha = f(\log n)$ for a semiconductor with a single sign of conductivity is governed by such a mechanism.

Thus, Dunayev [18] obtained similar results by preparing mechanical (physical) mixtures of various composition from powders of electron and hole PbS. It is possible to establish several causes for the formation of composite conductivity in Mg₃Sb₂.

1. The anisotropy of the energy zones of a crystal can lead to the simultaneous existence of electron and hole conductivity in a lattice, which, however, is hardly applicable to the given case since the anisotropy of such a kind would have been observed only for conductivity of the metallic type; that is, in the absence of the forbidden zone. The presence of the forbidden zone in the energy spectrum of electrons in the Mg₃Sb₂ phase we consider proved as given in this article and as revealed by the existence of the internal photoeffect, concerning which greater detail will be given in a separate article.

2. Semicrystalline samples of alloy can be a constant mechanical (physical) mixture of fine crystals with hole and electron conductivity which crystals are formed during the process of preparation of the samples because of the reaction's proceeding nonhomogeneously in the volume and because of the nonequilibrium distribution of excess Mg or Sb atoms in the lattice of the compound.

With the aim of clarifying such a possibility, we prepared several fine microsections of various Mg₃Sb₂ samples and carried out on them measurements of the sign of the thermoelectromotive force for separate individual portions of the microsections (microcrystals and intercrystalline layers) by means of a special microthermo-probe (sonder). The mobile electrode of the thermo-probe was manipulated by means of a micrometric screw under a microscope, on the stage of which the sample under study was fastened. A preliminary microphotograph was taken of

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the sample upon which (photograph) the signs of thermoelectromotive force were directly drawn for various portions of the sample. One of the photographs showed a sample of an alloy containing 50 weight-percent Mg and 50 weight-percent Sb. The large dark crystals observed represented intermetallic compound Mg_3Sb_2 . During an investigation with the thermo-probe all crystals showed a positive sign of thermoelectromotive force corresponding to hole conductivity. The remaining part of the alloy had electron conductivity. In a microphotograph of a sample of an alloy close in composition to the stoichiometry of Mg_3Sb_2 all the crystals visible possessed hole conductivity and only the narrow inter-crystal layers had electron conductivity. Such samples obviously cannot be considered completely homogeneous.

3. The crystals of the intermetallic compound can possess composite conductivity because of the simultaneous presence of local acceptor and donor levels.

The choice between mechanism 2 and mechanism 3 requires more detailed investigations conducted as far as possible on monocrystals.

In conclusion, we should like to note once more than further detailed study of the physical properties of intermetallic compounds of constant, or fixed, composition is of positive interest to possible technical applications, as well as to theory.

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[Appended figures follow.]

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Table 1. Compounds of Mg with Elements of the I-VII Groups

Zintl's Boundary						
I	II	III	IV	V	VI	VII
		Mg ₄ Al ₃ MgAl Mg ₂ Al ₄ MgAl ₃ Mg ₅ Ga ₂ Mg ₂ Ga MgGa MgGa _{1+x}	Mg ₂ Si	Mg ₃ P ₂	MgS	MgCl ₂
Mg ₂ Cu MgCu ₂	Mg ₇ Zn ₃ MgZn Mg ₂ Zn ₃ Mg ₂ Zn ₂ Mg ₂ Zn ₁₁	Mg ₂ In ₂ Mg ₂ In MgIn MgIn ₂ Mg ₅ Tl ₂ Mg ₂ Tl MgTl	Mg ₂ Ge	Mg ₃ As ₂	MgSe	MgBr ₂
Mg ₃ Ag MgAl	Mg ₃ Cd MgCd MgCd ₃		Mg ₂ Sn	Mg ₃ Sb ₂	MgTe	MgI ₂
Mg ₃ Au Mg ₅ Au ₂ Mg ₂ Au MgAu	Mg ₃ Hg Mg ₅ Hg MgHg MgHg ₂		Mg ₂ Pb	Mg ₃ Bi ₂		
Structures characteristic of metals and alloys			Structures characteristic of salt-forming compounds			
			Type CaF ₂	Type L ₂ O ₃	Type NaCl and ZnS	Type CdCl ₂ and CdI ₂

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Table 2.

No of Sample	Composition of Sample in Weight %		Excess of Metal Over Stoichio- metric Composi- tion in %	Specific Electrical Conductivity in /ohm-cm	ΔE in eV	Note
	Sb	Mg				
1	78.7	21.3	7.5	51.2		Sawn from bar
2	72.0	28.0	6.3	6.4		" " "
3	73.8	26.2	4.0	0.41		" " "
4	74.5	25.5	3.1	0.025		" " "
5	76.2	23.8	0.9	0.00081	0.47	" " "
6 (Ser VI)	76.8	23.2	0.2	0.032	0.43	Annealed 24 hr at 600°C Crystal sample
7 (Ser VII)	76.9	23.1	0.1	0.000025	0.58	Pressed annealed sample (600°C, 24 hr)
3 (Ser V)	77.4	22.6	1.9	7.85		Sawn from bar
1 (Ser VI)	75.35	24.65	1.77	0.56		" " "
3 (Ser VII)	76.6	23.4	0.4	0.016	0.36	Poorly homogenized coarse crystal sample
10 ()	--	--	--	0.00028	0.59	Homogeneous sample
7 ()	--	--	--	0.00035	0.72	" "

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Table 3

<u>No of Sample</u>	<u>ΔE_p in eV</u>	<u>ΔE in eV</u>
1 (crystalline)	0.03 ₅	0.66
7 (VII)	0.05 ₄	0.87
6 (VI)	0.02 ₀	0.68
3 (VII)	0.05 ₅	0.52
3 (V)	0.01 ₅	0.64
5 (sawn)	0.02 ₃	0.69

Table 4

<u>Sample</u>	<u>σ/ohm·cm</u>	<u>$\frac{\lambda}{\text{cal/cm} \cdot \text{sec} \cdot ^\circ\text{C}}$</u>
1	$0.77 \cdot 10^4$	0.0120
2	$0.36 \cdot 10^4$	0.0086
3	$0.30 \cdot 10^4$	0.0050
4	$0.22 \cdot 10^2$	0.0026
Mg	$22.4 \cdot 10^4$	0.37
Sb	$2.57 \cdot 10^4$	0.044

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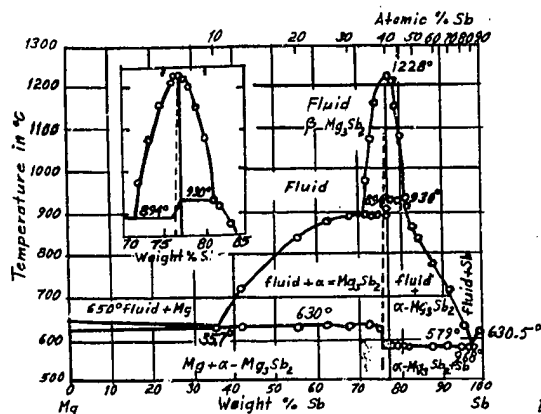


Figure 1

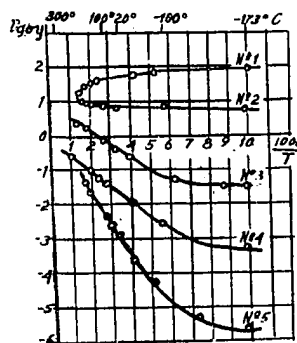


Figure 2

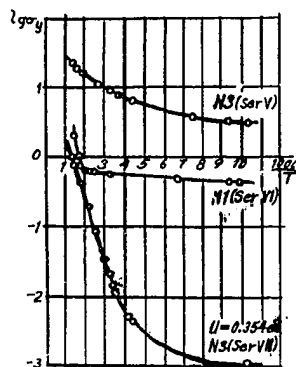


Figure 3

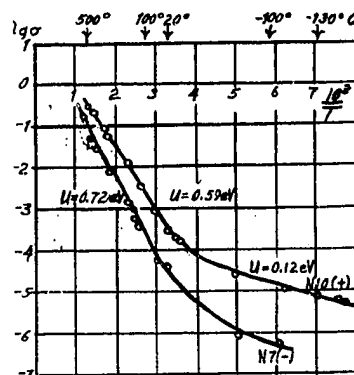


Figure 4

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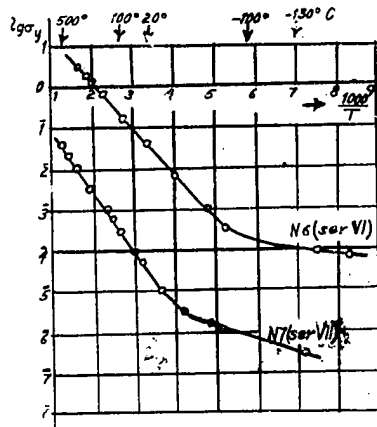


Figure 5

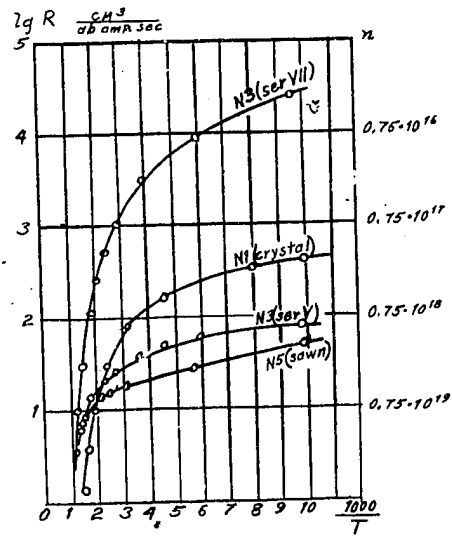


Figure 6

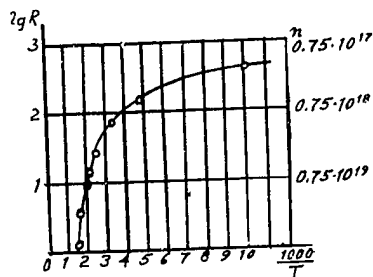


Figure 7. Crystalline Sample
No 1 Mg_3Sb_2 . Homogeneous
Sample.

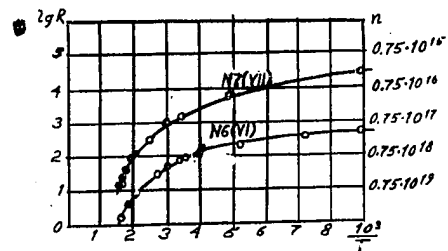


Figure 8

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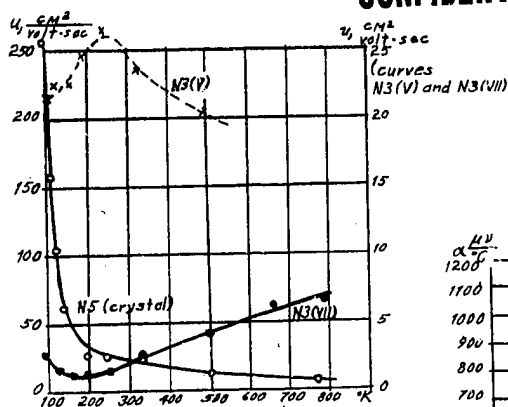


Figure 9

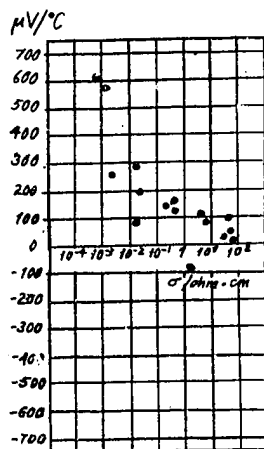


Figure 11

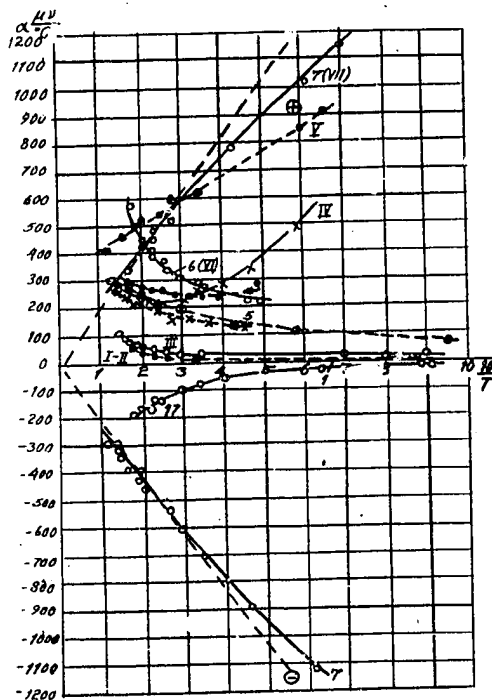


Figure 10

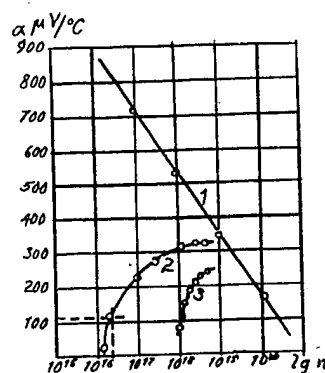


Figure 12. Comparison of Experimental Curves for Thermo-EMF with Theoretical. 1-Theoretical curve calculated according to Pisarenko's formula 2,3-Experimental curves

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